IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of	Confirmation No. 4833
IJPEIJ et al.	Atty. Ref.: 4662-147
Appln. No. 10/567,098	T.C. / Art Unit: 1713
Filed: February 3, 2006	Examiner: C.C. Lu

FOR: PROCESS FOR THE PREPARATION OF A METAL-ORGANIC COMPOUND COMPRISING AT LEAST ONE IMINE LIGAND

* * *

AMENDED APPEAL BRIEF UNDER 37 CFR § 41.37

August 13, 2009

Mail Stop Appeal Brief – Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Appellants submit this Amended Appeal Brief to appeal the Examiner's final rejection as set forth in the Office Action mailed January 9, 2009 (the "final Office Action") and also in response to the July 15, 2009 Notification of Non-Compliant Appeal Brief.

The Notification of Non-Compliant Appeal Brief was issued on July 15, 2009. Since August 15, 2009 is a Saturday, Applicants believe that the current Amended Appeal Brief, filed on the first working day after August 15, 2009, is timely. If any other fee is required to consider this Amended Appeal Brief, the undersigned authorizes the fee (or any deficiency therein) to be charged to Deposit Account 14-1140 under Order No. 4662-147.

Reversal of the Examiner's rejection of claims 1-5 and 11-15 by the Board of Patent Appeals and Interferences (the "Board") is respectfully requested.

I. REAL PARTY IN INTEREST

The assignee, DSM IP ASSETS B.V. holds all rights in the subject invention, as well as the invention disclosed and claimed therein, by assignment from the inventors.

II. RELATED APPEALS AND INTERFERENCES

Appellants, the assignee, and its legal representative do not know of any prior or pending appeal, interference, or judicial proceeding which is related to, directly affects or is directly affected by, or has a bearing on the Board's decision in this appeal.

III. STATUS OF CLAIMS

Claims 1-5 and 11-15 stand rejected. They are at issue in this appeal and listed in the Claims Appendix.

Claims 6-10 and 16 are objected to. They are not at issue in this appeal.

IV. STATUS OF AMENDMENTS

No amendment was filed subsequent to final rejection.

V. SUMMARY OF CLAIMED SUBJECT MATTER

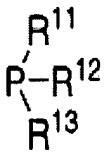
The invention involved in this appeal is directed to a process for the preparation of a metal-organic compound comprising at least one phosphinimine ligand (see

pending claim 1). The process comprising contacting a HA adduct of a phosphinimine ligand compound according to formula 1 with a metal-organic reagent of formula 2 in the presence of at least 2 equivalents of a base, wherein HA represents an acid, of which H represents its proton and A its conjugate base,

with **Y=N-H** as formula 1,

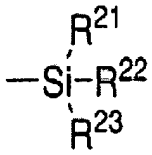
and $\mathbf{M^{v}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX}$ as formula 2,

and wherein Y is defined by the formula :



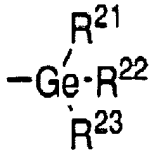
(formula 3)

wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

and a germanyl radical of the formula :



(formula 5)

wherein R^{2j} is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl and aryloxy radicals, each substituent R^{1j} or R^{2j} may be linked with another R^1 or R^2 to form a ring system,

and M represents a group 4 or group 5 metal ion

V represents the valency of the metal ion, being 3, 4 or 5

L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different,

k, l, m, n = 0,1, 2, 3, 4 with k+l+m+n+1=V, and

X represents a group 17 halogen atom.

This invention is supported by original claim 1 and in the Specification at the following locations: the Abstract; page 1 line 33 to page 2 line 18; page 3 line 27 to page 4 line 16; and page 6 lines 1-3.

Therefore, the invention as presently claimed is clearly supported by Appellants' disclosure as originally filed.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

A. Under 35 U.S.C. 103(a), was it proper to reject claims 1-5 and 11-15 as allegedly unpatentable over U.S. Patent 6,355,744 in view of CA 2,261,518?

VII. ARGUMENTS

Claims 1-5 and 11-15 should stand or fall together as one group.

35 U.S.C. 103 – Nonobviousness

A claimed invention is unpatentable if the differences between it and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art. *In re Kahn*, 78 USPQ2d 1329, 1334 (Fed. Cir. 2006) citing *Graham v. John Deere*, 148 USPQ 459 (1966). The *Graham* analysis needs to be made explicitly. *KSR v. Teleflex*, 82 USPQ2d 1385, 1396 (2007). It requires findings of fact and a rational basis for combining the prior art disclosures to produce the claimed invention. See id. ("Often, it will be necessary for a court to look to interrelated teachings of multiple patents . . . and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue"). The use of hindsight reasoning is impermissible. See id. at 1397 ("A factfinder should be aware, of course, of the distortion caused by hindsight bias and must be cautious of arguments reliant upon ex post reasoning"). Thus, a prima facie case of obviousness requires "some rationale, articulation, or reasoned basis to explain why the conclusion of obviousness is correct." *Kahn* at 1335; see *KSR* at 1396. A claim that is directed to a combination of prior art elements "is not proved obvious merely by demon-strating that each of its elements was, independently, known in the prior art." Id. Finally, a determination of prima facie obviousness requires a reasonable expectation of success. See *In re Rinehart*, 189 USPQ 143, 148 (C.C.P.A. 1976).

Claims 1-5 and 11-15 were rejected under Section 103(a) as allegedly being unpatentable over U.S. Patent 6,355,744 (cited as the '744 patent below) in view of Canadian Application 2,261,518 (cited as the CA'518 below).

In the final rejection, the Examiner alleges that it would have been obvious for a skilled artisan to employ CA'518's aminophosphonium halide to the '744 patent's phosphinimine ligand containing metal-organic compound preparation process. The Examiner further assumes that the aminophosphonium salt can be neutralized with a strong base as described on page 3, last paragraph of CA'518. The last paragraph on page 3 of CA'518 describes the use of bases such as NaOH, NaOMe and BuLi. The use of NaOH and NaOMe may appear to provide the phosphinimine at first glance. However, Appellants urge the Board to consider the fact that the use of MeOH is generally known to hydrolyze the phosphimine to the thermodynamically more stable and undesired phosphinoxide under liberation of $MeNH_2$ (Evidence Appendix, Exhibit 1: Hawkeswood et al., 84 Dalton Trans. 2182-87, (2005), second reaction in scheme 2, submitted in the Amendment and Response of December 5, 2008). Similar hydrolyzing reactions may be expected when NaOH and NaOMe are used to neutralize the aminophosphonium salt. Therefore, there is no reasonable expectation of success shown by the Examiner that a phosphimine would be produced by reacting the aminophosphonium salt with bases such as NaOH, NaOMe and BuLi.

Appellants submit that strong bases have to be extremely pure to prevent hydrolysis of phosphinimine. It is well known that e.g. KNPPh3 can only be made in an extremely dry environment. Mixtures that contain phosphinoxide are difficult to purify. In particular, BuLi is a very strong base that complicates selective formation of the NH-phosphinimine caused by deprotonation of the NH-phosphinimine to the NLi-phosphinimide, resulting again in separation problems. For the reasons stated above, one of ordinary skill in the art would not have employed CA'518's aminophosphonium

halide to the '744 patent's phosphinimine ligand containing metal organic compound preparation process since the prior art teaches against such as approach.

Furthermore, the Examiner's argument is based on the assumption that triethylamine is a stronger base than Y=N-H so that one would have expected that triethylamine would react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$. See, Final Office Action, sentence spanning pages 2 and 3 where the Examiner states, "Since triethylamine is a stronger base than Y=N-H, one would also have expected that the most common amine base, triethylamine, to react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$ and further deprotonates the phosphinimine to provide Y=N- to react with the metal-organic reagent of formula 3 to prduce the metal-organic compound." Appellants respectfully disagree with the Examiner's contention. In fact, standard organic chemistry textbooks contradicts the Examiner's assumption. It is commonly known that the pK value of Et_3N is 10.8 while the pK value of guanidine is 13.6. The pK value of guanidine is conservatively chosen as this is the lowest pK of the guanidine family. When substituted, the pK of the guanidine increases analogous to substitution of ammonia - where it is commonly known that the pK increases from 9 to 11. The value of the used phosphinimines is comparable to that of substituted guanidines since they are isoelectronic. Because of this, one of ordinary skill in the art would not have expected that triethylamine to react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$.

For this reason, the combination of U.S. Patent 6,355,744 and CA 2,261,518 does not render the claimed invention obvious, inter alia, because there is no

expectation that such a combination would cooperated in the manner proposed by the Examiner in the Final Office Action.

Appellants urge the Board to reverse the Section 103 rejection because their claimed invention would not have been obvious to one of ordinary skill in the art at the time it was made.

Conclusion

For the reasons discussed above, the Examiner's rejection is improper and they should be reversed by the Board. Appellants submit that the pending claims are in condition for allowance and earnestly solicit an early Notice to that effect.

Respectfully submitted,

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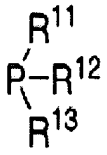
VIII. CLAIMS APPENDIX

1. A process for the preparation of a metal-organic compound, comprising at least one phosphinimine ligand, the process comprising contacting a HA adduct of a phosphinimine ligand compound according to formula 1 with a metal-organic reagent of formula 2 in the presence of at least 2 equivalents of a base, wherein HA represents an acid, of which H represents its proton and A its conjugate base,

with **Y=N-H** as formula 1,

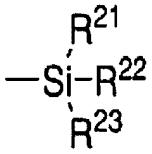
and $\mathbf{M^{v}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX}$ as formula 2,

and wherein Y is defined by the formula :



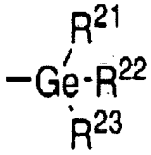
(formula 3)

wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8}alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

and a germanyl radical of the formula :



(formula 5)

wherein R^{2j} is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl and aryloxy radicals, each substituent R^{1j} or R^{2j} may be linked with another R^1 or R^2 to form a ring system,

and M represents a group 4 or group 5 metal ion

V represents the valency of the metal ion, being 3, 4 or 5
L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different,
k, l, m, n = 0,1, 2, 3, 4 with k+l+m+n+1=V, and
X represents a group 17 halogen atom.

2. A process according to claim 1, wherein the base is an organic base, an inorganic base or a metal-organic base.

3. A process according to claim 1, wherein the organic base is an amine or a phosphane.

4. A process according to claim 1, wherein the organic base is a dialkylamine, a trialkylamine, amonoarylamine, diarylamine or a triarylamine.

5. A process according to claim 1, wherein the base is triethylamine, pyridine, tripropylamine, tributylamine, 1, 4-diaza-bicyclo [2.2. 2] octane, pyrrolidine or piperidine.

11. A process according to claim 1 wherein the reaction is carried out in an aprotic solvent.

12. A process according to claim 11, wherein the solvent is the base.

13. Process for the preparation of a polyolefin which comprises polymerizing an olefin monomer in the presence of a metal-organic compound made according to the process of claim 1, wherein the base is an olefin polymerisation compatible base, which metal-organic compound is activated anywhere in, or before polymerisation equipment.

14. Process according to claim 13, wherein the metal-organic compound is used without purification.

15. Process according to claim 13, wherein the metal-organic compound is formed in the polymerisation equipment.

IX. EVIDENCE APPENDIX

Exhibit 1

Hawkeswood et al., Dalton Trans. 2182-87, 84 (2005)

FULL PAPER

Dalton
www.rsc.org/dalton

Syntheses and reactions of the bis-boryloxide $O(Bpin)_2$ (pin = $O_2C_2Me_4$)

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The reaction of the phosphine oxides, $OPEt_3$ **1** and $OPn\text{-}Bu_3$ **2** with pinacolborane (HBpin) results in phosphine oxide reduction and the formation of $O(Bpin)_2$ **3**. In contrast, the phosphine oxide $OPn\text{-}Bu_3$ reacts with $HB(C_6F_5)_2$ or $B(C_6F_5)_3$ to give only the donor–acceptor adducts. Compound **3** reacts with $HNPr\text{-}Bu_2$ to give the phosphinimonium borate salt, $[t\text{-}Bu_2PNH_2][(Bpin(OBpin)_2]$ **6**, while reaction with Cp_2ZrMe_2 affords the species $Cp_2Zr(OBpin)_2$ **7**.

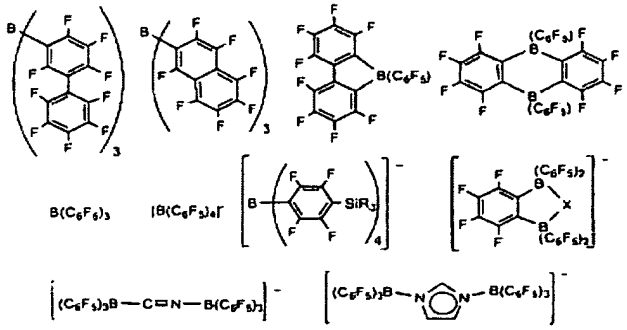
Introduction

The utility of methylalumoxane (MAO) as an activator for zirconocene olefin polymerization catalysts was discovered 25 years ago.[1] In this role MAO functions to alkylate early metal catalyst precursors and subsequently abstract an alkyl group to generate a coordinatively unsaturated metal cation and a weak or non-coordinating anion. The need to use typically 1000 equivalents of MAO to effect precatalyst activation as well as intellectual properties issues prompted researchers to seek alternative activators. Perhaps the most successful alternatives were developed by Exxon researchers in the 1980's and are based on Lewis acidic fluorinated-aryl-borane and the corresponding non-coordinating borates. More recently the research groups of Marks,[2–4] Piers,[10–11] and Bochmann[13] have developed a variety of more complex fluorinated B- and Al-based[16–18] Lewis acid activators and non-coordinating anions (Scheme 1). Nonetheless, the commercial use of many of creative developments are limited by the broad range of compounds defined in Exxon patents.[19–24] In our efforts, we have focused on the study of the fundamental reactivity of Group 13 compounds with the view that new reactivity will offer alternative avenues to activators or non-coordinating anions. To this end, we continue to explore the chemistry of boranes. In recent work, we have described the steric effects on the reaction pathways of phosphinimines and dialkoxyboranes.[25] Phosphinimines with sterically small substituents on P underwent reduction to the corresponding phosphine upon reaction with borane. In this manuscript, we probe the application of this finding to the reduction of phosphine oxides. The reaction of pinacolborane with phosphine oxides provides a facile and clean route to a bis-boryloxide which is readily converted to an unusual phosphinimonium bis-boryloxide-borate salt. Reactivity of the bis-boryloxide with dimethylzirconocene is also described and the implications regarding the potential utility of these compounds is considered.

Experimental

General data

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres glovebox. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. HBpin (pinacolborane), $Pn\text{-}Bu_3$, PEt_3, and N_3SiMe_3 were used as received from Sigma-Aldrich. Modified literature procedures were used to synthesize the phosphinimines.[26] ^1H, $^{11}B\{^1H\}$, ^{19}F, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance spectrometers. These spectrometers operate at either 300 or 500 MHz for ^1H NMR spectroscopy. Deuterated benzene and toluene were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents and freeze–pump–thaw-degassed (3×). C_6D_6 was used to record the NMR spectra unless otherwise indicated. For ^1H and $^{13}C\{^1H\}$ NMR spectra, trace amounts of protonated solvents were used as reference and NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra are referenced to 85% H_3PO_4, and $^{11}B\{^1H\}$ NMR spectra are referenced to $BF_3{\cdot}OEt_2$.



Scheme 1 Some B-based activators and non-coordinating anions

DOI: 10.1039/b504746d

and ^{19}F NMR spectra are referenced to CCl_3F. Combustion analyses were performed at the University of Windsor Chemical Laboratories.

Syntheses

Synthesis of OPR_3 (R = Et 1, *n*-Bu 2). These compounds were prepared in a similar fashion and thus one preparation is detailed. To neat $Et_3PNSiMe_3$ (4.0 g, 18.8 mmol) was added excess dry methanol (30 mL) *via* cannula at 25 °C. The resulting solution was refluxed for 16 h. The excess methanol, $MeOSiMe_3$ and $MeNH_2$ were removed *in vacuo* over a 6 h period. The product was crystallized from a pentane solution, dried *in vacuo* and recovered in 82% yield. 1: ^1H NMR (ppm): 1.16 (m, 6H, CH_2Me), 0.86 (m, 9H, Me); $^{31}P\{^1H\}$ NMR (ppm): 46.2; $^{13}C\{^1H\}$ NMR (ppm): 20.6 (d, PCH_2, $^1J_{P,C}$ = 65.8 Hz); 6.2 (s, Me). Calcd: H: 11.27%, C: 53.72%; Found: H: 11.16%, C: 53.58%. 2: 85% yield. ^1H NMR (ppm): 1.42 (m, 6H, PCH_2), 1.35 (m, 6H, $CH_2CH_2CH_2$), 1.23 (sextet, 6H, CH_2Me), $^3J_{H,H}$ = 4 Hz), 0.79 (t, 9H, Me, $^3J_{H,H}$ = 8 Hz); $^{31}P\{^1H\}$ NMR (ppm): 42.0; $^{13}C\{^1H\}$ NMR (ppm): 28.9 (d, PCH_2), $^1J_{P,C}$ = 32 Hz), 24.9 (d, $CH_2CH_2CH_2$), $^2J_{P,C}$ = 6 Hz), 24.7 (d, CH_2Me, $^3J_{P,C}$ = 2 Hz), 14.2 (s, Me). Calcd: H: 12.47%, C: 66.02%; Found: H: 12.49%, C: 65.98%.

Synthesis of $O(Bpin)_3$ 3.

Method (i). This method involves reaction of HBpin and one of **1**, **2** or $OPPh_3$, thus one such preparation is detailed. HBpin (0.344 mL, 2.73 mmol) was added *via* syringe to a solution of 1 (0.150 g, 1.13 mmol) in 25 mL of toluene. The solution was heated at reflux for 72 h. Toluene and Et_3P were removed *in vacuo* and the product was dissolved in minimal amounts of pentanes. A crystalline product precipitated at −33 °C and the supernatant was removed. The crystals of 3 were washed with cold pentanes, dried *in vacuo* and isolated in 92% yield. X-Ray quality crystals were obtained by recrystallization from pentanes at −33 °C.

Method (ii). $ONMe_3$ (0.129 g, 1.72 mmol) was added to a 100 mL Schlenk flask to which 40 mL of toluene was added. HBpin (0.5 mL, 3.45 mmol) was slowly added to the toluene slurry. The flask was put under static vacuum and stirred for 1 h. The solvent and NMe_3 were removed *in vacuo* and the resulting white solid was dried *in vacuo* for 16 h. The white solid was isolated in 96% yield. ^1H NMR (ppm): 1.00 (s, Me); $^{13}C\{^1H\}$ NMR (ppm): 83.3 (s, BOC), 25.0 (s, Me); $^{11}B\{^1H\}$ NMR (ppm): 21.6 ($\upsilon_{\frac{1}{2}}$ = 750 Hz). Calcd: H: 8.96%; C: 53.39%; Found: H: 8.85% C: 53.16%.

Synthesis of $(n\text{-}Bu_3PO)HB(C_6F_5)_2$ 4 and $(n\text{-}Bu_3PO)B(C_6F_5)_3$ 5. These compounds were prepared in a similar fashion and thus one preparation is detailed. To a solution of 2 (0.041 g, 0.188 mmol) in 3 mL of toluene, was added a solution of $HB(C_6F_5)_2$ (0.065 g, 0.188 mmol) in 3 mL of toluene. The solution was stirred for 72 h. The solvent was removed *in vacuo* and the product was obtained in 88% yield. 4: ^1H NMR (ppm): 1.30 (m, 6H, PCH_2), 1.00 (m, 12H, $CH_2CH_2CH_2Me$), 0.67 (t, 9H, Me, $^3J_{H,H}$ = 7 Hz), $^{31}P\{^1H\}$ NMR (ppm): 76.7; $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, ppm): 25.1 (d, $^1J_{P,C}$ = 64 Hz), 24.0 (d, $^2J_{P,C}$ = 15 Hz), 23.2, 13.3; ^{11}B NMR (ppm): −12.7; ^{19}F NMR (ppm): −136.5, −159.7, −165.3. Calcd: H: 5.00%, C: 51.09%; Found: H: 4.88%, C: 51.01%. 5: 87% yield. ^1H NMR (ppm): 1.28 (m, 6H, PCH_2), 0.91 (m, 12H, $CH_2CH_2CH_3$), 0.62 (t, 9H, Me, $^3J_{H,H}$ = 7 Hz); $^{31}P\{^1H\}$ NMR (ppm): 71.8; $^{13}C\{^1H\}$ NMR (ppm): 148.8 (d(m), $^1J_{C,F}$ = 242 Hz, C_6F_5 (*o*-C)), 140.7 (d(m), $^1J_{C,F}$ = 249 Hz, C_6F_5 (*p*-C)), 138.0 (d(m), $^1J_{C,F}$ = 249 Hz, C_6F_5 (*m*-C)), 25.3 (d, PCH_2CH_2, $^1J_{P,C}$ = 66 Hz), 24.2 (d, $CH_2CH_2CH_3$), $^2J_{P,C}$ = 16 Hz), 23.3 (s, CH_2CH_2Me), 13.5 (s, CH_2Me); $^{11}B\{^1H\}$ NMR (ppm): −2.7 (br); ^{19}F NMR (ppm): −134.0, −157.7, −164.1. Calcd: H: 3.73%, C: 49.34%; Found: H: 3.72%, C: 48.82%.

Synthesis of $[t\text{-}Bu_2PNH_2][(Bpin(OBpin)_2]$ 6. Solid 3 (0.03 g, 0.11 mmol) was added to a solution of tBu_2PNH (0.024 g, 0.11 mmol) in 2 mL of pentane. A white solid precipitated from the pentane solution immediately. The mixture was stirred for 2 h and set aside to allow the solid to settle in the vial. The pentane soluble product ($tBu_2PNBpin$) was decanted off and the solid was washed twice with 2 mL of pentane. The product was dried *in vacuo*, resulting in a fine white powder in 80% yield. X-Ray quality crystals grew from a toluene solution. ^1H NMR (partial, ppm): 1.11 (d, 27H, *t*-Bu, $^3J_{P,H}$ = 12 Hz), 1.11 (br s, 36H, BOCMe); $^{31}P\{^1H\}$ NMR (ppm): 61.9; $^{13}C\{^1H\}$ NMR (partial, ppm): 39.5 (d, *t*-Bu, $^1J_{P,C}$ = 45 Hz), 29.6 (s, *t*-Bu), 26.5 (s, OCMe), 25.3 (s, OCMe). $^{11}B\{^1H\}$ NMR (ppm): 21.9, 9.3. Calcd: C: 57.08%, H: 10.39%, N: 2.21%; Found: C: 57.23%, H: 10.40%, N: 2.23%.

Synthesis of $Cp_2Zr(OBpin)_2$ 7. To a solution of 3 (0.106 g, 0.398 mmol) in 25 mL of toluene was added solid Cp_2ZrMe_2 (0.050 g, 0.199 mmol). The solution was refluxed for 16 h, followed by removal of toluene and MeBpin *in vacuo*. The solid was washed three times with pentane, dissolved in a minimal amount of toluene and stored at −33 °C. Crystalline material precipitated from the pentane solution, the supernatant was decanted off, and the product was dried *in vacuo*. A white crystalline solid was collected in 82% yield. X-Ray quality crystals were obtained by recrystallization from pentane at −33 °C. ^1H NMR (ppm): 6.15 (s, 10H, Cp), 1.14 (s, 24H, Me); $^{13}C\{^1H\}$ NMR (ppm): 114.3 (s, Cp), 81.3 (s, BOC), 25.4 (s, Me); $^{11}B\{^1H\}$ NMR (ppm): 19.2. Calcd: H: 6.75%, C: 52.08%; Found: H: 6.79%, C: 51.85%.

X-Ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 second exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45$–$50.0°$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package. See Table 1 for crystallographic data.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[17] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the case of 3 the oxygen and chelate carbon atoms are disordered and were modelled with two orientations. For 7 disorder of the pinacolate chelates were modelled with two orientations of the O and C atoms in the chelate ring. In these cases the fractional atoms were refined isotropically and the hydrogen atoms for the pinacolate methyl groups were not included. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined with the exception of the phosphinammonium protons in 6 which were located and refined. The locations of the largest peaks *in the final difference*

Table 1 Crystallographic data

Crystal	3	6	7
Molecular formula	$C_{12}H_{28}B_2O$	$C_{30}H_{63}B_3NO_3P$	$C_{22}H_{44}B_2O_4Zr$
Formula weight	269.93	631.23	507.33
a/Å	6.544(4)	10.752(3)	20.276(11)
b/Å	21.289(13)	13.737(4)	13.162(8)
c/Å	11.767(7)	14.181(4)	19.540(11)
α/°	90	94.422(6)	90
β/°	95.599(12)	104.550(6)	100.694(13)
γ/°	90	106.244(6)	90
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
V/Å^3	1631.5(17)	1921.9(9)	5124(5)
D_{calc}/g cm^{-3}	1.099	1.091	1.315
Z	4	2	8
μ/mm^{-1}	0.081	0.114	0.461
θ range/°	1.91–23.27	1.50–23.32	1.85–23.29
Reflections	6727	8994	10468
Data $F_o^2 > 3\sigma(F_o^2)$	2340	5469	3687
Parameters	253	394	260
R^a	0.0974	0.0854	0.0942
R_w^b	0.2677	0.1554	0.2410
Goodness of fit	0.884	0.843	1.031

Data collected at 20 °C with Mo-Kα radiation (λ = 0.71069 Å). [a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{\frac{1}{2}}$.

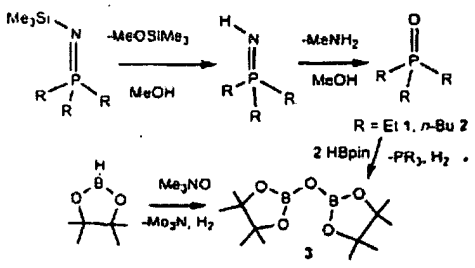
Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

CCDC reference numbers 266791–266793.

See http://www.rsc.org/suppdata/dt/b5/b504246a/ for crystallographic data in CIF or other electronic format.

Results and discussion

The alcoholysis of *N*-trimethylsilylphosphinimines is a firmly established route to *N*-H-phosphinimines.[26,28–32] While this reaction has been exploited extensively for the preparation of sterically bulky phosphinimines, the alcoholysis of less bulky phosphinimines to *N*-H-phosphinimines has been shown to be more sensitive, requiring the use of lower temperatures (−30 °C).[33] Herein, the analogous reactions of sterically unencumbered *N*-trimethylsilylphosphinimines at 25 °C are shown to result in the further transformation of *N*-H-phosphinimines to the corresponding phosphine oxides. In this fashion, the phosphine oxides, $OPEt_3$ **1** and $OPn\text{-}Bu_3$ **2** were obtained from the precursors $R_3PNSiMe_3$. The spectral data and elemental analyses confirmed the formulations of the products, **1** and **2**. The impact of steric effects on the reaction pathways in the protonolyses is reminiscent of those recently described for the reactions of phosphinimines and pinacolboranes where small substituents prompted P–N bond cleavage. By analogy, the close approach of the sterically unencumbered electropositive P atom and an alcohol O atom presumably prompts the transformation to phosphine oxide (Scheme 2).



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The reactions of pinacolborane with the tertiary phosphine oxides **1**, **2** or $OPPh_3$ were conducted in refluxing toluene for 72 h. $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy on the crude reaction mixture suggested the complete conversion to the corresponding tertiary phosphine and the formation of a single boron-containing compound **3**. The boron-containing product was the same in each of these three reactions. In the case of the reaction of **1**, the volatility of PEt_3 resulted in its facile removal by vacuum affording **3** cleanly in 92% yield. For the corresponding reaction of **2**, removal of $Pn\text{-}Bu_3$ was effected *via* precipitation of **3** from pentane at −33 °C giving **3** in 65% yield. Finally in the case of the reaction of $OPPh_3$ filtration through Celite and removal of pentane yielded **3** in 75% yield. X-Ray crystallography (Fig. 1) and ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy were consistent with the formulation of **3** as $O(Bpin)_2$.

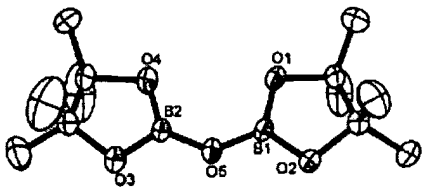

Fig. 1 ORTEP drawing of **3**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered oxygens and chelate carbons are shown.

X-Ray crystallographic data for **3** confirmed the formulation and revealed that although there was significant disorder of the oxygen positions, the average B–O bond distances for the bridging oxygen atom was 1.36(2) Å while the B–O–B′ angle in **3** was found to average 136(2)°. These bond distances are similar to those observed in the related boryloxides $O(B(terphenyl)_2)_2$ (1.340(2) Å and 1.347(2) Å),[34] $O(B(Cl)(N\text{-}Pr_2)_2)_2$ (1.367(3) Å and 1.367(3) Å),[35] $O(B(N_2(Ph)_2C))_2$ (1.365(4) Å and 1.370(4) Å)[36] and $O(B(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_2)_2$ (1.370(2) Å and 1.359(2) Å).[37] The disorder of the pinacolate chelate rings precludes direct comparison with the related species $(Bpin)_2$[38] and $(Bpin)_2(OCMe_2CMe_2O)$.[39] The overall geometry of **3** is reminiscent of that recently reported for the species $HN(Bpin)_2$ where the B–N–B angle was found to be 132.9(3)°. However the B–O distances in **3** are significantly shorter than the B–N distance in $HN(Bpin)_2$ (1.419(6) Å).[25]

Several alternative syntheses of **3** were also uncovered. Prolonged reflux of pinacolborane in toluene (144 h), afforded numerous products including **3** which was isolated in 13% yield. An efficient route to **3** was shown to involve the reaction of Me_3NO with pinacolborane at 25 °C (Scheme 2), which affords **3** in 96% isolated yield. Similar reactions of trialkyl- or triarylboranes with amine oxides reported by Köster and Morita were shown to give trialkoxy- or triphenoxyboranes.[40] Similarly, reactions of species containing B–H bonds with amine-oxides afforded boryl-hydroxides. Thus, the reaction of pinacolborane and phosphine oxide or amine oxide is consistent with the proposed mechanism that results in reduction of the phosphine oxide or amine oxide and generation of the transient boryl-hydroxide species HOBpin which reacts immediately with excess borane to give **3**. A similar mechanism involving transient boryl-hydroxides has been previously suggested for the oxidation of organoboranes with amine oxides.[40]

Other researchers have probed reductions of Group 15 and Group 16 elements with boranes. Some years ago, Köster and Morita showed that $OPPh_3$ is reduced by B_2Pr_4, BPr_3, BEt_2H and $B(NR_2)_3$,[41] although these reactions result in multiple boron-containing products. More recently, reduction of OPR_3 has been shown to occur in the presence of excess $BH_3\text{-}SMe_2$, producing phosphine-borane adducts.[42,43] In addition, the deoxygenation of sulfoxides (R_2SO) to sulfides effected by reaction with

Table 1 Crystallographic data

Crystal	3	6	7
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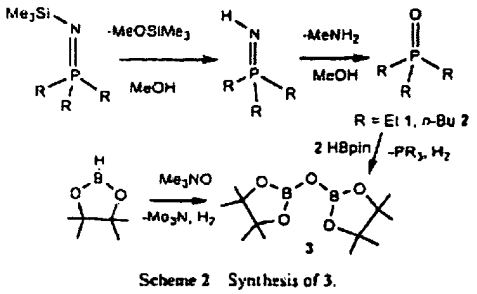

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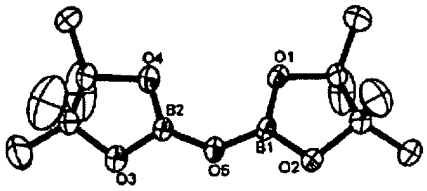

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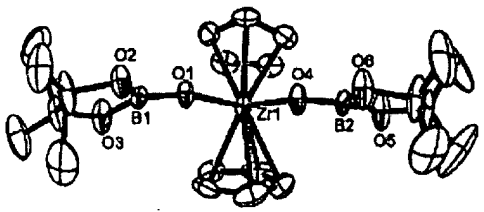
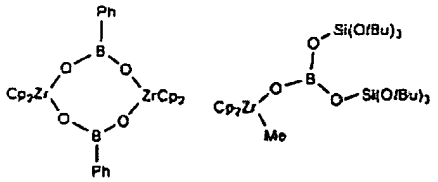


Fig. 3 ORTEP drawing of 7, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered chelate carbons are shown. Selected distances (Å) and angles (°): Zr(1)–O(4) 2.011(9), Zr(1)–O(1) 2.025(8), O(1)–B(1) 1.291(16), O(2)–B(1) 1.311(17), O(3)–B(1) 1.400(17), O(4)–B(2) 1.280(15), O(5)–B(2) 1.360(16), O(6)–B(2) 1.357(16); O(4)–Zr(1)–O(1) 97.6(3), B(1)–O(1)–Zr(1) 156.0(9), B(2)–O(4)–Zr(1) 154.2(9), O(2)–B(1)–O(3) 108.6(13), O(5)–B(2)–O(6) 108.3(12).

Zr–O bond distances of 2.011(9) Å and 2.025(8) Å with a O–Zr–O' angle of 97.6(3)°. In comparison, the Zr–O bond distances and O–Zr–O' bond angles in the zirconocene–alkoxide species, $Cp_2Zr(\mu\text{-}OCH_2CMe_2CH_2O)_2ZrCp_2$ and $Cp_2Zr(\mu\text{-}OCH_2C_6H_4CH_2O)_2ZrCp_2$ are 1.945(6) Å, 1.946(6) Å, 101.4(3)° and 99.4(1)°, respectively.[55] The longer Zr–O bond length in 7 is consistent with the presence of the Lewis acidic boron center. The larger angles at Zr in the zirconocene–alkoxides may be an artifact of the macrocyclic nature of these complexes. The B–O bond distances were determined to be 1.291(16) Å and 1.280(15) Å with Zr–O–B bond angles of 156.0(9)° and 154.2(9)°. In addition, the Bpin units are canted with respect to the ZrO_2 plane by only 18.0° and 5.7° respectively. This geometry places the acceptor B p-orbital approximately orthogonal to a vacant a_1 molecular orbital on Zr, thus providing for strong Zr–O and B–O π-bonding and accounting for the increase in the angle at O.

Previous reports regarding the chemistry of boryloxides have been sparse over the last 15 years. The groups of Power, Chisholm, Gibson and Serwatowski have utilized boryloxide ligands to form metal complexes of Li, Co, Mn, Fe, Al, Zn and Cd.[56-62] In addition only two examples of Zr complexes containing boryloxide ligands have been reported. Balkwill *et al.* have described the bimetallic complexes $(Cp_2Zr(\mu^2\text{-}O_2BAr))_2$ (Ar = Ph, C_6H_3-2,4,6-Me_3, C_6F_5) (Scheme 5),[63] synthesized *via* reaction of Cp_2ZrMe_2 with $ArB(OH)_2$ generated *via* hydrolysis of $(OBAr)_3$. These macrocyclic species exhibit shorter average Zr–O (1.985(2) Å) bonds and longer average B–O (1.350(6) Å) bonds. At the same time, the Zr–O–B angles range from 141.8(2)° to 156.7(2)° for the derivatives with Ar = Ph, C_6H_3-2,4,6-Me_3. The upper limit of this range is similar to the Zr–O–B angles seen in 7, but presumably the macrocyclic nature of these complexes accounts for the lower end of this range. More recently, Tilley's group has also reported the structure of the related boryloxide derivative $Cp_2ZrMe(OB(OSi(O\text{-}Bu)_3)_2)$ (Scheme 5).[64] The Zr–O distance of 1.974(4) Å is slightly shorter than those in 7 while the bridging B–O bond distance and Zr–O–B angle are slightly larger at 1.329(3) Å and 160(2)°, respectively. These metric perturbations are consistent with the steric demands of the boryloxide substituents in $Cp_2ZrMe(OB(OSi(O\text{-}Bu)_3)_2)$.



Scheme 5 Known Zr–boryloxide species.

The facile formation of 7 from the reaction of Cp_2ZrMe_2 and 3 is thought to be initiated by interaction of the Lewis acidic B center with the Zr-bound methyl group. This prompts simultaneous formation of MeBpin and transfer of the boryloxide ligand to Zr. Presumably this process repeats to give 7. All attempts to intercept the intermediate in this process were unsuccessful. This chemistry reflects both the acidity of the B centers and the reactivity of the B–O bonds in 3. Thus, while the reactivity shown herein affords a new synthetic route to a B-based anion, the lability of the B–O bonds makes these boryloxides unsuitable for use as activators or non-coordinating anions. Efforts are underway to utilize this unique synthetic route to prepare related boryloxide salts in which the B–O bond strengths are enhanced by the introduction of electronically favorable and sterically demanding substituents. The results of these efforts will be reported in due course.

Acknowledgements

Financial support from NSERC of Canada, NOVA Chemicals Corporation is gratefully acknowledged. SH is grateful for the award of an OGS scholarship.

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X. RELATED PROCEEDINGS APPENDIX

None.